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㉖ **Black surface treated steel sheet and method for its production.**

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㉗ A colored zinc composite-plated steel sheet which comprises a steel sheet or a plated steel sheet, a colored composite-plating film comprising zinc and an oxide of a coloring metal such as nickel, cobalt, iron, chromium, tin or copper and provided on the steel sheet at a coverage of 0.1-5 g/m<sup>2</sup> and a transparent guard coat having a thickness of 3 μm or less provided on the film is obtained by carrying out electrolysis in an acidic aqueous solution containing zinc ions, coloring metal ions and nitrate ions, nitrite ions, perchlorate ions, chlorate ions and/or condensed phosphate ions and having a pH of 1-4 using the steel sheet or plated steel sheet as a cathode at a current density of 5-100 A/dm<sup>2</sup> and a current quantity of 20-200 coulomb/dm<sup>2</sup>.

## BLACK SURFACE TREATED STEEL SHEET AND METHOD FOR ITS PRODUCTION

This invention relates to a colored steel sheet, especially a black sheet, used for members to be decorated and a method for its production.

Development for surface treated steel sheets of low cost and high performance has been earnestly demanded in the fields of rust proofing steel sheets for cars, household steel sheets, household furnishings and building materials. These demanded standards have been yearly shifted to further lower cost and higher quality and steel makers have developed new techniques and new products to meet the requirements of users. Recently, it has been attempted to provide precoated steel sheets instead of the conventional surface treated steel sheets which are subjected to working and then pretreatment and coating, whereby the pretreatment and coating which have been made by users can be omitted and products of high quality can be obtained at low cost. For meeting these requirements, hitherto there have been used precoated steel sheets provided with a coating composition, but now demands for inorganic colored steel sheets have become greater for complete cost-down, sophisticated appearance and for improving weldability and removing damages caused by handling.

For color tone, need for blackish colors is strong and besides the above requirements, the following are required: namely, fingerprints are not left thereon; high workability, chemical resistance and corrosion resistance.

The conventional black treating method is generally applied to stainless steel, steel sheets, and copper, but since zinc plated steel sheets meet the object of this invention from the point of cost and corrosion resistance, conventional technique for blackening thereof will be explained below.

As known blackening methods of zinc or zinc alloy plated steel sheets, there is the method of JP-A-45544/77 which comprises treating the sheets in an aqueous chromate solution containing silver ions (black chromate), the method disclosed in Jitsumu Hyomen Gijutsu, Vol. 32, No. 10, pages 541-542, Tables 3 and 5, and the like. According to these methods, silver oxide is coprecipitated together with a chromate film to obtain black surface. JP-A-65139/77 discloses a method which forms a black appearance by production of a sulfide. JP-A-151490/83 and 151491/83 disclose blackening by anode electrolysis treatment. According to the former, an oxide of Ni, Co or Mo is produced by anodization in an alloy plating bath of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  or  $\text{Mo}^{2+}$  and  $\text{Zn}^{2+}$  and according to the latter, the oxide is produced by anodization of Ni, Co or Mo and Zn alloy plated steel in an aqueous ammonium sulfate solution. Furthermore,

JP-A-121275/85 discloses a method for obtaining black appearance by chemically dissolving an Ni-Zn alloy plated steel sheet with an aqueous solution of nitric acid or a chlorate.

Moreover, JP-A-200996/85 discloses a method for blackening by cathodic electrolysis in an alloy plating bath containing  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  to obtain a steel sheet plated with a zinc alloy containing at least 15% of Ni.

The above mentioned conventional methods suffer from many problems. For example, the method using silver ions is expensive and besides has a difficulty in productivity. The anodization method has the problem that the plated metal of the base is greatly dissolved and so the metals to be plated are limited and besides once plated metal may be redissolved.

The method of JP-A-200996/85 has also the problems in the production that since the resulting film is an Ni-Zn alloy black plating film, there are limitations in current density and bath temperature for attaining black and substrate plating is limited to zinc or zinc alloy plating.

The object of this invention is to provide a black surface treated steel sheet free from the above problems and produced by a black treating method which can be carried out at high speed in a short time and has no limitations in the substrate metals.

According to this invention, there is provided a colored zinc composite-plated steel sheet which has thereon 0.1-5 g/m<sup>2</sup> of a colored composite-plating film mainly composed of metallic zinc or a zinc alloy and a coloring metal oxide or hydrated oxide and obtained by electrolysis with a steel sheet or a plated steel sheet as a cathode in an acidic aqueous solution mainly composed of  $\text{Zn}^{2+}$  ions and coloring metal ions represented by  $\text{Me}^{n+}$  and strongly oxidizing ions represented by  $\text{OX}^-$  and a chemical treatment film and a transparent guard coat film of 3  $\mu\text{m}$  or less in thickness.

According to this invention, there is further provided a method for making a colored zinc composite-plated steel sheet which comprises carrying out electrolysis with a steel sheet or a plated steel sheet as a cathode in an acidic aqueous solution mainly composed of  $\text{Zn}^{2+}$  ions and coloring metal ions represented by  $\text{Me}^{n+}$  and strongly oxidizing ions represented by  $\text{OX}^-$  at a current density of 5-100 A/dm<sup>2</sup> and a current amount of 5-200 coulomb/dm<sup>2</sup>, then washing the treated sheet and thereafter applying a guard coat.

Fig. 1 is a diagram which show the coloring mechanism and construction of a film according to this invention.

Figs. 2(a), 2(b), 2(c) and 2(d) are diagrammatic sectional views which show the construction of the colored zinc composite-plated steel sheet of this invention.

Fig. 3 and Fig. 4 are microphotographs of the surface of the black surface treated steel sheet of this invention. Fig. 3 shows a sample obtained in a bath containing condensed phosphoric acid and Fig. 4 a sample obtained in a bath without condensed phosphoric acid.

This invention is based on the technique of cathodic composite deposition composed of black oxides or hydrated oxides of Zn and Me and metallic zinc or zinc alloy on a metal surface. Hitherto, poor plating has been observed in blackish color plating such as zinc plating due to phenomena such as discoloration caused by coarse crystal of plated metals. The quality of the plating is not uniform and utterly unsatisfactory and this technique has never been practically employed. This invention has succeeded in producing a uniform blackish film of superior adhesiveness by interaction of an alloy plating bath and an oxidizing ion.

The most important point of this invention is that the conditions for forming a colored film and the quality of the film can be markedly improved by adding a strongly oxidizing water-soluble anion to a zinc alloy plating bath containing a metal ion which forms a black oxide or hydrated oxide. This invention will be explained in detail below.

The composition of the color surface treated steel sheet of this invention and the mechanism of formation of the film will be explained.

In the treating bath there are present zinc ions ( $\text{Zn}^{2+}$ ), blackening metal ions ( $\text{Me}^{n+}$ ), strongly oxidizing ions ( $\text{OX}^-$ ) and ( $\text{H}^+$ ).

As shown in Fig. 1, zinc and a zinc alloy are deposited on the cathode due to the reduction of  $\text{Zn}^{2+}$  and  $\text{Me}^{n+}$ . At the same time, the metals are oxidized with  $\text{OX}^-$  in the plating bath simultaneously with the deposition and zinc oxide (mark +) and MeO (mark ●) are deposited. These oxides also include hydrated oxides. Generation of hydrogen is prevented by deposition of the zinc at a high hydrogen overvoltage.

As  $\text{Me}^{n+}$ , there may be used  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Sn}^{2+}$  and  $\text{Cu}^{2+}$  alone or in combination which cause coloration upon oxidation with  $\text{OX}^-$ .  $\text{OX}^-$  is a strongly oxidizing anion and is at least one of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{ClO}_4^-$ , and  $\text{ClO}_3^-$ . In the bath of this invention, condensed phosphoric acid ions, for example, ions represented by  $\text{P}_2\text{O}_7^{2-}$ ,  $\text{P}_2\text{O}_4^{4-}$ ,  $\text{P}_3\text{O}_{10}^{5-}$  and  $\text{P}_6\text{O}_{18}^{4-}$ ,  $\text{Cr}^{3+}$  and a brightener (coating improver) may also be used to improve the quality of the film.

In this invention, zinc acts as a vehicle for the colored composite-plated film. If the composite ratio of the oxide and zinc is improper, the film is apt to become susceptible to the subsequent chemical treatment and guard coat application, resulting in powdering in the surface layer. A colored film good in adhesion properties can be produced by selecting a proper  $\text{Me}^{n+}/\text{Zn}^{2+}$  ratio and suitable oxidizing ability pH of the bath and the current density.

When a coating improver is added to the plating bath, the resulting composite-plating film becomes dense and is improved in its quality.

Fig. 2 is a diagrammatic sectional view of the color surface treated steel sheet. S indicates a metallic substrate as a base which may be a thin steel sheet, stainless steel sheet, and various plated steel sheets such as, for example, a zinc or zinc alloy plated steel sheet, an aluminum or aluminum alloy plated steel sheet, a tin plated steel sheet and a lead plated steel sheet, etc. B indicates a colored zinc composite-plating layer, G indicates a guard coat, Gc indicates a chemical treatment film in a part of the guard coat, for example, a chromate film and Z indicates a plating layer.

Fig. 2(a) shows an example of a colored steel sheet with a guard coat, Fig. 2(b) an example of a colored plated steel sheet, Fig. 2(c) an example of a chromate treated, colored, plated steel sheet after coloration with a guard coat and Fig. 2(d) an example of a chromate treated, colored steel sheet with a guard coat.

The colored film of this invention is a composite film of a metal and a coloring compound (oxide or hydrated oxide) and the degree of coloration depends on the deposited amount of the oxide or hydrated oxide. The amount of at least 0.1 g/m<sup>2</sup> is necessary for obtaining a black appearance. A deposition amount of at least 1.0 g/m<sup>2</sup> is desirable for a blackish appearance.

When the composite plating film is too thick, a phenomenon called powdering occurs and thus the thickness is suitably 5 g/m<sup>2</sup> or less.

The chemical treatment may be effected immediately after formation of the black film by electrolysis. The chemical treatment includes the chromate application method comprising application of a chromate solution mainly composed of a water-soluble chromium compound and then drying without water washing, the chromate etching method comprising reaction with a chromate solution and then water washing, the electrolytic chromate method comprising electrolysis in a chromate solution and phosphate treatment with a solution composed of phosphoric acid or a condensed phosphoric acid compound. The chromate treatment tends to increase blackness and is advantageous for obtaining a black appearance.

When a solution containing condensed phosphate ions is used as a coating improver, the resulting black film comprises a metal oxide and phosphates. The black film is in the form of a smooth film having fine irregularities and according to this film there may be very easily obtained a black appearance of 20 or less in terms of value L (brightness: JIS Z 8370).

5 Fig. 3 is a scanning electron micrograph (SEM) of the surface of a black surface treated steel sheet obtained by subjecting the surface of a steel sheet to plating with zinc at a thickness of 3  $\mu\text{m}$  and thereafter to a cathodic electrolysis treatment in an aqueous solution of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}/\text{NiSO}_4 \cdot 7\text{H}_2\text{O}/\text{NaNO}_3/\text{Na}_5\text{P}_3\text{O}_{10} = 200/100/10/16$  g/l having a pH = 1.8 at a current density of 10 A/dm<sup>2</sup> and at a current quantity of 50 coulomb/dm<sup>2</sup> and then to washing with water. Fig. 4 is a scanning  
10 electron micrograph of a black surface treated steel sheet obtained under the same conditions as above except that  $\text{Na}_5\text{P}_3\text{O}_{10}$  was not added to the bath. It is clear that the surface of the sheet obtained without  $\text{Na}_5\text{P}_3\text{O}_{10}$  has a rod-like rough structure while that of the sheet obtained with addition of  $\text{Na}_5\text{P}_3\text{O}_{10}$  has a fine dense structure. However, the rod-like rough structures can be also improved by higher current density and additives such as  $\text{Cr}^{3+}$ , or a brightener.

15 The composition of the black film comprises oxides or hydrated oxides of Zn and at least one of Me (Fe, Co, Ni and Cr, etc.) and metallic zinc and it may include a phosphate or a brightener. The phosphate is an amorphous condensed phosphate and is different from the conventional crystalline phosphate film. Sufficient blackness (20 or less in value L) can be obtained by depositing the film in an amount of at least 0.1 g/m<sup>2</sup> for the common zinc electroplated steel sheet, Ni-Zn alloy electroplated steel sheet and cold-rolled  
20 steel sheet, though it depends on the surface state of the metal to be treated. When the deposition amount is too large, the film suffers from the powdering phenomenon, resulting in poor adhesion. A practical upper limit of the deposition amount is 5 g/m<sup>2</sup>. In case of a black color, the most preferred is 1.0 - 3.0 g/m<sup>2</sup>.

The colored zinc composite-plated steel sheet of this invention has a guard coat on the colored composite-plating film. This guard coat is provided for improvement of quality. For example, the application  
25 of the guard coat affords an improvement in the uniformity of the appearance and an increase in the degree of coloration.

Steel sheets having an appearance of from semi-gloss to gloss can be obtained depending on the kind and thickness of the guard coat. Further, scratch resistance is improved by the guard coat. The guard coat is especially effective for protection against pressing, handling and mars caused by striking. Corrosion  
30 resistance is especially highly improved.

The guard coat of this invention includes (1) a chemical coating film such as a chromate film, phosphate film, chelate film and the like which are formed with a chemical reaction, (2) a resin film, (3) an inorganic polymer film, (4) a composite film of a resin and an inorganic polymer, (5) oils, fats, waxes, etc. It may  
35 comprise one or a plurality of these films.

The thickness of the guard coat must be determined not so as to damage appearance and weldability. It is at most 3  $\mu\text{m}$ , preferably 1.5  $\mu\text{m}$  or less in total thickness. The resin coating weight of the guard coat is 3 g/m<sup>2</sup> or less, preferably 1.5 g/m<sup>2</sup> or less.

The resin film (organic polymer) is a film formed by coating a water-soluble, water-dispersible or solvent soluble organic high molecular weight compound together with a hardener and hardening the coat by  
40 baking or by coating composite polymers comprising inorganic and organic compounds and a hardener, if necessary, and hardening the coat by baking. The inorganic and organic compounds include inorganic compounds, e.g., chromium compounds, oxides such as silica, titania, alumina and zirconia, silicate minerals such as mica and talc, phosphates and borates, organic compounds such as fatty acid soaps, carbon, fatty acid esters and plastic particles and organometallic compounds such as silane coupling agents  
45 and titanium coupling agents.

The inorganic polymers include silicate compounds and sols such as sodium silicate and lithium silicate, condensed phosphoric acid polymers, polyphosphates, zirconic acid polymers. Oil, and fat waxes may be known ones.

In the colored zinc composite-plated steel sheets of this invention, since the colored composite-plating  
50 film and the guard coat are thin in thickness, there can be obtained appearance and quality utilizing the surface state of the substrate metal such as gloss and roughness. For example, semigloss appearance can be obtained by employing an average surface roughness of the substrate metal of 1.5  $\mu\text{m}$  or more. Gloss appearance can be obtained by an average surface roughness of the substrate metal of 1  $\mu\text{m}$  or less.

A method for the production of the colored coated steel sheet of this invention is explained below.

55 Zinc ions play an important part in the acidic aqueous solution used in this invention. The zinc ion is reduced to zinc, and zinc oxide or hydrated oxide is deposited on the cathode, and metallic zinc prevents generation of hydrogen, imparts rust proofness and simultaneously acts as a binder for the film and improves the current efficiency and affords a uniform appearance.

The concentration of the zinc ions as  $Zn^{2+}$  may be within the range of 10-100 g/l and is preferably 20-50 g/l.

$Me^{n+}$  in the acidic aqueous solution is at least one selected from the group consisting of  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $Sn^{2+}$  and  $Cu^{2+}$  and the addition amount thereof is 10-100 g/l, preferably 20-80 g/l.

5 The proper ratio of  $Me^{n+}/Zn^{2+}$  in the solution is between 0.1-8.0. A lower ratio of  $Me^{n+}/Zn^{2+}$  gives a coarser and more black structured film and a higher ratio gives a compact and glossy one.

As source of supply of  $Zn^{2+}$  and  $Me^{n+}$ , there may be used sulfates, chlorides, phosphates, sulfamates and sulfonates and as sources of replenishment, there may be used carbonates, oxides, hydroxides, metallic powders, etc.

10  $OX^-$  is an ion selected from  $NO_3^-$ ,  $NO_2^-$ ,  $ClO_4^-$  and  $ClO_3^-$  and is supplied as a soluble salt or acid. The concentration of  $OX^-$  is suitably 1-50 g/l and most suitably 3-20 g/l as ion. When it is less than 1 g/l, the amount of oxide formed is not enough to give coloration and no coloration occurs. When it is more than 50 g/l, all metals are oxidized to make it difficult to get an adherent film and the powdering phenomenon is apt to occur.

15  $OX^-$  is reduced at the cathode, but oxidized at the anode. It should be replenished in case of shortage.

A colored deposition can be obtained easily by electrolysis in the solution mainly composed of  $Zn^{2+}$ ,  $Me^{n+}$  and  $OX^-$ . However, to improve the quality of the deposition, condensed phosphoric acid compounds may be added.

20 The condensed phosphoric acid compounds are compounds which provide ions where 2 or more P are combined, such as  $P_2O_5^{4-}$ ,  $P_3O_9^{5-}$ ,  $P_4O_{10}^{6-}$  and  $P_6O_{18}^{8-}$ , for example, sodium salts, potassium salts, calcium salts, magnesium salts, metal salts (Zn, Fe, Co, Ni, Cr). The amount of the condensed phosphoric acid compound to be added is 1-20 g/l.

25 The condensed phosphoric acid compound used in this invention provides a smooth finishing of the black film deposited. It will be recognized from comparison of Fig. 3 and Fig. 4 that the condensed phosphoric acid has a great effect. The black film becomes smooth and dense by the action of the condensed phosphoric acid compound. Thus, the surface becomes semigloss whereby the appearance is improved and besides, adhesion and corrosion resistance are remarkably improved. The condensed phosphoric acid compound has the further action of enhancing the adhesiveness to the guard coat by coexisting as a phosphate in the film.

30 Besides of its action as a color element, the  $Cr^{3+}$  ions in the solution also act as improver like the condensed phosphoric acid compound. In this case, the  $Cr^{3+}$  is added in an amount of 0.1-1.0 g/l, preferably 0.1-1 g/l as a phosphate, sulfate, chloride, carbonate and chelate compound. When the concentration is less than 0.1 g/l, the improving effect is low and when it is more than 10 g/l, a sufficiently black color tone cannot be obtained. Films obtained from an aqueous solution containing these ions, are precipitated as a Cr compound with the colored film to improve the corrosion resistance and the adhesion after application of the guard coat.

35 The coloration can be attained at bath temperatures in a wide range, but preferred bath temperature is 30-60°C.

40 The colored film obtained by this invention can be improved in quality, especially gloss, powdering and adhesion to the guard coat by using an acidic aqueous solution containing a brightener in addition to  $Zn^{2+}$ ,  $Me^{n+}$  and  $OX^-$ .

45 As examples of the brightener, mention may be made of water-soluble polymeric compounds, for example, polyamine compounds of cationic quaternary ammonium salts, polyaminesulfone compounds, nonionic polyacrylamide compounds, copolymers of these compounds with anionic compounds and known brighteners such as aldehydes or phenolic compounds and sulfonic acid compounds.

The amount of the brightener depends on the kind of the compounds and it may be added optionally within the range of 10-40000 ppm.

50 When a condensed phosphate ion is used, the pH of the aqueous solution is preferably 1.0-4.0. According to this invention, a black surface can be obtained at a pH of a very wide range (0.7-4.0), but the above pH range is preferred considering the quality of the resulting black film, e.g., adhesion. When the pH is less than 1, hydrogen gas is generated and causes uneven coloration. When it is more than 4, precipitation is apt to occur. A pH of 1.5-3.0 is preferred considering the powdering phenomenon and the adhesion to the guard coat.

55 The bath temperature is preferably 20-60°C, though coloration is possible in a wide range of temperature.

Next, the electrolysis conditions will be explained below.

The method of this invention is a very excellent method which can select wide conditions for coloring as compared with the conventional methods. The current density is 10-100 A/dm<sup>2</sup>. When it is less than 10 A/dm<sup>2</sup>, coloring is difficult. When it is more than 100 A/dm<sup>2</sup>, hydrogen gas is generated and there is the high possibility of removal of the formed film. The current density has an influence on the quality of the composite film. A higher current density gives a more compact structure with a metal rich layer. A lower current density gives a more coarse structure and an oxide rich layer. The preferable range of the current density which provides best quality (appearance, adhesion, corrosion resistance) is 20-50 A/dm<sup>2</sup>. The quantity of the current is 20-200 coulomb/dm<sup>2</sup>. When it is less than 20 coulomb/dm<sup>2</sup>, coloration is difficult, resulting in uneven appearance. When it is more than 200 coulomb/dm<sup>2</sup>, removal of the film and pinholes often occur due to generation of hydrogen gas and besides, a white film is sometimes deposited to cause uneven coloration. When a condensed phosphate is used, the quantity of current is desirably 5-100 coulomb/dm<sup>2</sup> for the same reasons.

With reference to the flow velocity, both of a still bath or a bath of high flow velocity may be employed.

The method of this invention has been applied to cold-rolled steel sheet, zinc alloy plated steel sheet, zinc plated steel sheet, gloss zinc plated steel sheet, tin plated steel sheet, etc. A colored film could be formed on all of them and in case of a black film, the cold-rolled steel sheet and zinc alloy plated steel sheet were superior in blackness and scratch resistance.

In this invention, if necessary, other compounds may be added to the bath for the following purposes, namely, various supporting salts for enhancing electroconductivity of the solution; borates, phosphates and phthalates as pH buffers; polymers for improving adhesion workability; phosphates, chromic acid, inorganic sol compounds, cationic polymers for rust proofing or enhancing adhesion to the guard coat; chelating agents for prevention of precipitation; chlorides and fluorides for imparting smoothness to the zinc composite-plating film formed.

The coating of the guard coat can be performed by known methods such as roll coating, squeeze roll coating, spraying, air knife drawing, dipping, electrolysis, electrostatic coating, etc. If necessary, the thus coated guard coat is then heated (hot air, infrared, combustion furnace, electric heat) or hardened with ultraviolet rays.

This invention will be explained by the following examples. Unless otherwise notified, Zn<sup>2+</sup> and Me<sup>n+</sup> were made from a sulfate and a sodium salt was used for OX<sup>-</sup>.

The current density is indicated by DK and expressed by A/dm<sup>2</sup>. The quantity of current is indicated by Q and expressed by coulomb/dm<sup>2</sup>. The amount of colored zinc composite-plating deposited is indicated by CW and measured by the gravimetric method and expressed by g/m<sup>2</sup>.

The value L shows brightness and was measured by a commercially available differential colorimeter. A value L of 25 or less is necessary in connection with the degree of blackness.

Unless otherwise notified, the following chemical treatment and application of the guard coat were effected in the examples.

As chromate, a coating type chromate comprising silica and chromic acid (with addition of phosphoric acid according to the purpose) was used in a deposition amount of 20 mg/m<sup>2</sup> in terms of Cr. As the guard coat there was used a clear coat of a commercially available aqueous olefin acrylic acid emulsion and silica sol. The coat was applied by the roll coat method and baked with hot air at a sheet temperature of 120°C so that a coat of about 1 μm was obtained.

The adhesion was measured by subjecting the sample to flexural working of T-bending (one sheet thickness) of 180° and then to peeling by a tape or by Erichsen 10 mm deep drawing and then peeling by a tape. The results were evaluated visually and rated as follows:

- "◎" —No peeling occurred.
- "○" —A slight peeling occurred.
- "Δ" —Tape adhered in the form of dots.
- "x" —Complete peeling occurred.

The corrosion resistance was evaluated by the continuous salt spray exposure test specified in JIS Z 2371 and the results are shown by the time required for formation of 5% of rust per unit area.

#### Example 1

A cold-rolled steel sheet was subjected to electric zinc plating in a sulfuric acid bath by a known method, then washing with water, immediately thereafter the coloring treatment as shown in Table 1, then application of a guard coat and baking. The electrolysis treatment was carried out using the sample as a cathode and a lead plate as an anode.

After the coloring treatment, the sample was washed with water and dried with hot air and then the value of L was measured with a differential colorimeter.

Nos. 1-4 show the data obtained when sodium nitrate was used as  $\text{OX}^-$  and the ratio  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  was changed and indicate that low values of L were obtained with a bath containing  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$ .

5 Nos. 5-8 show the data obtained when a bath containing  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}$  was used and the current density was changed between 10-100 A/dm<sup>2</sup> and indicate that the value of L somewhat increased at 10 A/dm<sup>2</sup> and peeling in the form of dots began to occur at 100 A/dm<sup>2</sup>. No. 9 is an example where a pH of 1.2 was employed and a low value of L was obtained even at low pH. No. 10 shows an example where  $\text{OX}^-$  was not contained and only a high value of L was obtained.

10 Nos. 11 and 12 are examples where composite baths were used and low values of L were obtained.

Nos. 13-16 show the data obtained when the concentrations of  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}$  were changed. When the concentration of  $\text{Zn}^{2+}$  was too low, the film became white and when the ratio of the concentrations was close to 3, the value of L became high.

No. 17 shows the data obtained when a composite bath containing  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  as  $\text{Me}^{n+}$  was used and the influence of  $\text{Fe}^{3+}$  was small.

15 Nos. 18-20 are examples where  $\text{NO}_2^-$ ,  $\text{ClO}_4^-$ ,  $\text{ClO}_3^-$  and  $\text{Fe}^{3+}$  were used as  $\text{OX}^-$ . They show that  $\text{NO}_2^-$  and  $\text{ClO}_3^-$  which are less oxidizing afforded a somewhat higher value of L than  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ .

20 Nos. 21-22 are examples where  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  were jointly added as  $\text{Me}^{n+}$  and the pH was changed. They show that the value of L was high at around pH = 1, resulting in the etching phenomenon and uneven coloration.

Nos. 23-28 are examples where the concentration of  $\text{NO}_3^-$  as  $\text{OX}^-$  was changed. They show that the baths containing 50 and 100 g/l of  $\text{NO}_3^-$  gave high values of L and these were critical values. Concentrations of  $\text{NO}_3^-$  of 5, 10 and 20 g/l gave satisfactory values of L.

25 Nos. 29-31 are examples where the coulomb amount was changed. They show that when a current of 25 coulomb was used, the value of L was somewhat high and when 200 coulomb were used, powdering occurred.

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Table 1

No.		Zn <sup>2+</sup>	Me <sup>n+</sup>	OX <sup>-</sup>	pH	Bath temp.	Dk	Q	CW	Value L	Adhesion	Corrosion resist- ance
1	Comparative Example	50	Ni <sup>2+</sup> 0	NO <sub>3</sub> <sup>-</sup> 10	2.0	50	50	50	1.0	70	⊙	-
2	Example of this invention	"	10	"	"	"	"	"	1.5	25	⊙	300
3	"	"	20	"	"	"	"	"	1.6	11	⊙	"
4	Comparative Example	0	50	"	"	"	"	"	0.7	60	x	-
5	Example of this invention	50	Fe <sup>2+</sup> 20	"	"	"	"	"	1.6	20	⊙	300
6	"	"	"	"	"	"	10	"	"	25	⊙	"
7	"	"	"	"	"	"	75	"	"	12	⊙	"
8	"	"	"	"	"	"	100	"	"	12	Δ	72
9	"	"	"	"	1.2	"	50	"	"	12	⊙	300
10	Comparative Example	"	"	-	2.0	"	"	"	1.2	40	⊙	-
11	Example of this invention	"	Ni <sup>2+</sup> 20 Co + 2	NO <sub>3</sub> <sup>-</sup> 20	1.8	"	"	"	1.5	13	⊙	300

(To be cont'd)



Table 1 (Cont'd)

No.		Zn <sup>2+</sup>	Me <sup>n+</sup>	OX <sup>-</sup>	pH	Bath temp.	DK	Q	CW	Value L	Adhesion	Corrosion resistance
12	Example of this invention	"	Cr <sup>3+</sup> 5 Fe <sup>2+</sup> 20	NO <sub>3</sub> <sup>-</sup> 20	1.8	50	50	50	1.5	20	⊙	300
13	"	50	Fe <sup>2+</sup> 10	"	1.8	"	"	"	1.5	15	⊙	300
14	"	"	20	"	"	"	"	"	1.6	11	⊙	300
15	"	20	20	"	"	"	"	"	1.0	30	Δ	300
16	"	20	100	"	"	"	"	"	0.5	40	⊙	-
17	Example of this invention	50	Fe <sup>2+</sup> 20 Fe <sup>3+</sup> 5	"	"	"	"	"	1.4	18	⊙	300
18	"	75	Fe <sup>2+</sup> 20	NO <sub>2</sub> <sup>-</sup> 20	"	"	"	"	1.0	20	⊙	200
19	"	"	"	ClO <sub>4</sub> <sup>-</sup> 20	"	"	"	"	1.5	16	⊙	168
20	"	"	"	ClO <sub>2</sub> <sup>-</sup> 20	"	"	"	"	1.0	25	⊙	168
21	"	75	Ni <sup>2+</sup> 45	NO <sub>3</sub> <sup>-</sup> 20	3.0	"	"	"	1.5	12	Δ	300
22	"	"	Co <sup>2+</sup> 2	"	1.0	"	"	"	1.0	19	⊙	200

(To be cont'd)

Table 1 (Cont'd)

No.		Zn <sup>2+</sup>	Me <sup>n+</sup>	OX <sup>-</sup>	pH	Bath temp.	Dk	Q	CW	Value L	Adhesion	Corrosion resistance
23	Comparative Example	75	Fe <sup>2+</sup> 30	NO <sub>3</sub> <sup>-</sup> 0	1.5	50	60	50	1.0	50	-	-
24	Example of this invention	"	"	5	"	"	"	"	1.5	19	⊙	300
25	"	75	"	10	"	"	"	"	1.5	12	⊙	"
26	"	"	"	20	"	"	"	"	1.5	12	Δ	"
27	"	"	"	50	"	"	"	"	1.2	25	Δ	"
28	Comparative Example	"	"	100	"	"	"	"	1.0	30	Δ	"
29	Example of this invention	"	Ni <sup>2+</sup> 25 Co <sup>2+</sup> 5	NO <sub>3</sub> <sup>-</sup> 10	1.5	"	"	25	0.6	20	⊙	300
30	"	"	"	"	"	"	"	100	2.5	14	⊙	300
31	"	"	"	"	"	"	"	200	5.0	14	Δ ~ ⊙	300

## Example 2

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Electrolysis (50 A/dm<sup>2</sup> and 50 coulomb/dm<sup>2</sup>) was effected in an aqueous solution containing 400 g/l of zinc sulfate (Zn<sup>2+</sup> 92), 100 g/l of nickel sulfate (Ni<sup>2+</sup> 20) and 20 g/l of NaNO<sub>3</sub> and having a pH of 1.5 and a bath temperature of 50°C using a lead sheet as anode and various steel sheets and plated steel sheets as shown in Table 2 as cathode. Then, the thus treated steel sheets were provided with a guard coat in the

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Table 2

No.		Steel sheet to be treated	C.W	Value L	Adhesion	Corrosion resistance
32	Example of this invention	Cold-rolled steel sheet	1.6	11	◎	24
33	"	Stainless steel sheet	1.6	11	◎	-
34	"	Hot dipped zinc plated steel sheet (20 $\mu$ )	1.7	19	◎	168
35	"	Molten aluminum plated steel sheet (10 $\mu$ )	1.4	18	◎	500
36	"	Zn-Ni alloy electro-plated steel sheet	1.7	11	◎	500
37	"	(Ni 12%) 3 $\mu$				
38	"	Zn-Fe alloy electro-plated steel sheet	1.7	11	◎	500
39	"	(Fe 20%) 3 $\mu$				
40	"	Tern plated steel sheet	1.7	11	◎	500
41	"	Copper plated steel sheet	1.5	11	◎	500

According to the treating method of this example, there was a little dependency on the metals to be treated and the steel sheets and plated steel sheets could be satisfactorily colored.

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### Example 3

12% Ni-Zn electroplated steel sheets were treated in the same manner as in Example 2 except that solution A comprising the acidic aqueous solution used in Example 2 and 8000 ppm of a commercially available polyaminesulfone polymer and a solution B comprising the acidic aqueous solution used in Example 2 and 20 ppm of polyacrylamide were used. As a result, when solution A was used, the value of L was 11 and when solution B was used, the value of L was 12 and in both the cases there were obtained black steel sheets having semigloss and excellent in workability.

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### Example 4

Cold-rolled steel sheets were subjected to zinc-nickel alloy plating (Ni 12%) at 20 g/m<sup>2</sup> in a sulfuric acid bath by a known method, then coloring treatment as shown in Table 3, thereafter, chromate treatment and guard coat treatment.

No. 42 is an example where Ni<sup>2+</sup> was added as Me<sup>n+</sup> and Nos. 43-47 are examples where the bath contained Ni<sup>2+</sup> and Fe<sup>2+</sup> as Me<sup>n+</sup>. In only No. 47, pH was increased to 2.5. In all of these examples, black appearance and practically satisfactory qualities were obtained. Among them, the best adhesion was obtained by the bath containing two kinds of ions jointly added as Me<sup>n+</sup> and having low pH.

No. 48 is an example of Me<sup>n+</sup> being Fe<sup>2+</sup> and Nos. 49 and 50 are examples of using baths containing jointly Ni<sup>2+</sup> and Co<sup>2+</sup> and Fe<sup>2+</sup> and Cr<sup>3+</sup>, respectively. No. 51 is an example of using a bath containing no Me<sup>n+</sup>. It shows that the degree of blackness was insufficient and adhesion was poor. No. 52 is an example of using a bath having a low Ni<sup>2+</sup>/Zn<sup>2+</sup> ratio of 0.67. It shows that the adhesion was insufficient.

Nos. 53-56 are examples where the kind of OX<sup>-</sup> was changed. They show that NO<sub>3</sub><sup>-</sup> provided the lowest value of L and other oxidizing ions also had the blackening effect.

Nos. 57 and 58 are examples using baths containing jointly Fe<sup>2+</sup> and Sn<sup>2+</sup> or Cu<sup>2+</sup> and Nos. 59-61 are examples where the amount of Zn<sup>2+</sup> was changed to examine effect of the ratio Me<sup>n+</sup>/Zn<sup>2+</sup>. They show that when Zn<sup>2+</sup> was too low, ununiform appearance was apt to be formed.

No. 62 is an example of using a bath containing no Zn<sup>2+</sup>. It shows that a high value of L resulted and ununiform appearance was formed due to generation of gas.

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Table 3

No.		Bath composition (g/l)				pH	Bath temp.
		Zn <sup>2+</sup>	Me <sup>n+</sup>	Me/Zn	OX <sup>-</sup>		
42	Example of this invention	45	Ni <sup>2+</sup> 66	1.47	NaNO <sub>3</sub> 5	1.5	40
43	"	45	Ni <sup>2+</sup> 45 Fe <sup>2+</sup> 45	2.0	"	1.4	40
44	"	"	"	"	"	"	"
45	"	"	"	"	"	"	"
46	"	"	"	"	"	"	"
47	"	"	"	"	"	2.5	"
48	"	"	Fe <sup>2+</sup> 90	"	"	1.8	"
49	"	"	Ni <sup>2+</sup> 66 Co <sup>2+</sup> 5	"	"	1.8	"
50	"	"	Fe <sup>2+</sup> 90 Cr <sup>3+</sup> 5	"	"	1.8	"
51	Comparative Example	45	0	0	"	1.8	"

(To be cont'd)

(Cont'd)

52	Example of this invention	45	Ni <sup>2+</sup> 30	0.67	NaNO <sub>3</sub> 5	1.8	40
53	"	45	Ni <sup>2+</sup> 45 Fe <sup>2+</sup> 45	2.0	Zn(NO <sub>3</sub> ) <sub>2</sub> 7H <sub>2</sub> O 8.5	1.4	"
54	"	"	"	2.0	NaNO <sub>2</sub> 5	1.4	"
55	"	"	"	"	NaClO <sub>4</sub> 10	"	"
56	"	"	"	"	Na <sub>2</sub> ClO <sub>3</sub> 10	"	"
57	"	"	Fe <sup>2+</sup> 66 Sn <sup>2+</sup> 5	1.57	HNO <sub>3</sub> 3.6	"	"
58	"	"	Fe <sup>2+</sup> 66 Cu <sup>2+</sup> 2	1.51	HNO <sub>3</sub> 3.6	"	"
59	"	20	Fe <sup>2+</sup> 45 Ni <sup>2+</sup> 45	4.5	NaNO <sub>3</sub> 10	"	"
60	"	11	"	8.1	" 10	"	"
61	"	5	"	8.0	" 10	"	"
62	Comparative Example	0	"	∞	" 10	"	"

(To be cont'd)

(Cont'd)

Electrolysis		CW	Value L	Adhesion	Corrosion resistance	Uniformity
Dk	Q					
15	50	0.9	20	○	300	○
15	10	0.15	35	⊙	300	"
"	25	0.4	18	⊙	300	"
"	50	0.8	14	⊙	300	"
"	200	3.0	12	Δ	300	"
"	"	4.5	12	Δ	300	"
"	50	1.0	20	○	300	"
"	50	1.0	20	○	300	"
"	50	1.0	20	○	300	"
"	"	1.0	50	x	-	"

(To be cont'd)



	1.5	"	1.5	20	Δ	-	"
	"	50	0.8	14	⊙	300	"
	"	"	0.8	20	⊙	300	"
	"	"	0.7	20	⊙	300	"
	"	"	0.4	20	⊙	300	"
	"	"	1.0	20	○	300	"
	"	"	1.0	16	○	300	"
	"	"	0.6	14	⊙	300	"
	"	"	0.3	20	⊙	"	x
	"	"	0.2	25	⊙	"	"
	"	"	0.1	35	⊙	"	"

### Example 5

Electrolysis (20 A/dm<sup>2</sup> and 50 coulomb/dm<sup>2</sup>) was effected in an aqueous solution containing 45 g/l of Zn<sup>2+</sup>, 44 g/l of Ni<sup>2+</sup> and 43 g/l of Fe<sup>2+</sup> (Me<sup>n+</sup>/Zn<sup>2+</sup> = 1.93) and 5 g/l of NaNO<sub>3</sub> and having a pH of 1.4 using a lead sheet as an anode and various steel sheets and plated steel sheets as shown in Table 4 as cathode. Then the thus treated sheets were subjected to chromate treatment and application of a guard coat.

Table 4

No.		Steel sheet treated	C.W	Value L	Ad- hesion
63	Example of this inven- tion	Cold-rolled steel sheet	0.9	11	⊙
64	"	Stainless steel sheet	0.9	11	⊙
65	"	Hot dipped Zn plated steel sheet 20 $\mu$	0.8	20	⊙
66	"	Hot dipped Al plated steel sheet 10 $\mu$	0.8	20	⊙
67	"	Zn-Ni alloy elec- troplated steel sheet	0.8	11	⊙
	"	(Ni 12%) 3 $\mu$			
68	"	Zn-Fe alloy elec- troplated steel sheet	0.8	12	⊙
	"	(Fe 20%) 3 $\mu$			
69	"	Tern plated steel sheet	0.9	12	⊙
70	"	Copper plated steel sheet	0.9	10	⊙

The treatment of this example had a little dependency on the metals to be treated and all of the steel sheets and plated steel sheets could be colored.

#### Example 6

12% Ni-Zn alloy plated steel sheets (20 g/m<sup>2</sup>) were colored in black using the same acidic aqueous solution and electrolysis conditions as used in Example 5. The sheets were then subjected to a cathodic electrolytic chromate treatment (3 A/dm<sup>2</sup> and 10 coulomb/dm<sup>2</sup>) in an aqueous chromic acid solution of CrO<sub>3</sub>/SO<sub>4</sub> = 20/0.15 g/l (bath A) or CrO<sub>3</sub>/H<sub>3</sub>PO<sub>4</sub> = 20/0.15 g/l (bath B), were then coated with a commercially available composite coating composition comprising a polyethyleneimineacrylic acid emulsion and silica sol at a thickness of 1  $\mu$ m (as dry film) and baked at 120°C.

The resulting value of L was 12 in case of bath A and 11 in case of bath B and adhesion in both cases was such that no peeling was recognized in the test of T Bend (one sheet thickness).

#### Example 7

Cold-rolled steel sheets were subjected to bright and dull finish rolling of 0.6, 1.2 and 2.0  $\mu$ m in average roughness (Ra), then to common pretreatment and 12% Ni-Zn alloy plating (20 g/m<sup>2</sup>) and to the blackening treatment of Example 3, followed by the chromate treatment and guard coat treatment (1.5  $\mu$ m in film thickness) of Example 1. For the sheets of 1.2  $\mu$ m in average roughness, the thickness of the guard coat was 2, 3 and 5  $\mu$ m. The results are shown in Table 5.

Table 5

No.	Average roughness	Guard coat	Value L	Gloss	Adhesion	Spot weldability
71	0.6	1.5	10	50	⊙	⊙
72	1.2	1.5	12	25	⊙	⊙
73	2.0	1.5	13	19	⊙	⊙
74	1.2	2	11	25	⊙	○
75	1.2	3	10	30	⊙	Δ
76	1.2	5	10	40	⊙	x

## Evaluation of Spot Weldability

## Test Conditions:

Weldable Electric Current Range  
more than 3kA

1 - 3kA

0.5 - 1kA

impossible

Diameter of Welding Electrode: 4.5 mm

Pressure: 125 kg

Cycle: 10 Hz

⊙

○

Δ

x

Furthermore, the resulting sheets were subjected to spot welding by a conventional method to find that the sheet having a guard coat of 3  $\mu$ m showed poor current flowing and the welding was impossible for the sheet of 5  $\mu$ m in thickness of the guard coat.

## Example 8

12% Ni-Zn electroplated steel sheets were subjected to the same treatment as in Example 5 except that a solution A comprising the acidic aqueous solution used in Example 5 to which 8000 ppm of a commmer ally available polyaminesulfone was added and a solution B comprising the acidic aqueous solution used in Example 5 to which 20 ppm of polyacrylamide was added were used. Black steel sheets superior in adhesion with a value of  $L=11$  when solution A was used and a value of  $L=12$  when solution B was used were obtained.

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## Example 9

Electrolysis treatment was conducted in the aqueous solution as shown in Table 6 using a lead plate as anode and the following steel sheets as cathode: cold-rolled steel sheet (called S), zinc electroplated steel sheet (E), Ni(20%)-Zn alloy plated steel sheet (Z) and Fe(20%)-Zn alloy plated steel sheet (FZ). The treated sheets were washed with water and thereafter, if necessary, subjected to chemical treatment and coating with an organic polymer film. The quality of these sheets was evaluated.

No.77 which is outside the scope of this invention is an example of a black film obtained using a bath containing  $Zn^{2+}$  alone to which components C and D were added and when a guard coat was applied, a uniform appearance with a low value of  $L$  (12) was obtained, but when the guard coat was not applied, the value of  $L$  increased. No. 78 which is outside the scope of this invention is an example where component D was not added and adhesion was not sufficient. Nos. 79-86 are examples of this invention where the bath contained both  $Zn^{2+}$  and  $Ni^{2+}$  with components C and D changed in concentration and besides Dk was changed. In all of these examples black surface treated steel sheets of good quality were obtained. Nos. 87 and 88 are examples where the pH of the bath was 1.5. Nos. 89 and 90 are examples where cold-rolled steel sheets were subjected to the blackening treatment. In No. 90, adhesion was poor when the amount of deposition was 5.5. Nos. 91-93 are examples where zinc electroplated steel sheets were subjected to the blackening treatment and good results were obtained in all of them. As is seen in No. 93, a black film of a value of  $L=13$  was obtained with 12 coulomb/dm<sup>2</sup> and the quantity of current necessary for blackening was small. No. 94 is an example where an iron-zinc alloy plated steel sheet was subjected to the blackening treatment.

## Example 10

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12% Ni-Zn alloy plated steel sheets were subjected to the electrolysis treatment in the same manner as in Example 9 in an aqueous solution as shown in Table 7 and the treated steel sheets were provided with a guard coat, if necessary. An evaluation of the quality was effected.

No. 95 is an example of this invention where a bath containing both  $Zn^{2+}$  and  $Ni^{2+}$  and besides F ( $NaNO_3$ ) and H ( $Na_5P_3O_{10}$ ) was used. No. 96 is an example where a bath containing  $Zn^{2+}$  and  $Fe^{2+}$  together with F and H was used and No. 97 is an example where a bath containing  $Co^{2+}$  in addition to  $Zn^{2+}$  and  $Ni^{2+}$  was used. No. 98 is an example where  $Co^{2+}$  was replaced with  $Cr^{3+}$  in No. 97. The products of Nos. 95-98 had all black surface treated films of good quality. No. 99 is an example where  $NaNO_3$  and  $KClO_4$  were used in combination as oxidizing ion, No. 100 is an example where  $Na_5P_3O_{10}$  was used as condensed phosphoric acid and No. 101 is an example where both  $Ni^{2+}$  and  $Fe^{2+}$  were present in the bath. In these examples, products of good quality were obtained. No. 102 is an example where the pH of the bath was increased and the resultant product was inferior in adhesion and uniformity while the product of No. 103 where the pH was lowered was good in these properties. No. 104 is an example where Dk was 70 A/dm<sup>2</sup> and the appearance was uneven. Nos. 105-107 are examples where the  $Ni^{2+}/Zn^{2+}$  ratio was changed to 0.33-2.0 and the product of No. 105 was somewhat inferior in uniformity of appearance.

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## Example 11

The surface of cold-rolled sheets was electroplated with zinc ( $20 \text{ g/m}^2$ ) from a sulfuric acid solution, then subjected to cathodic electrolysis treatment in the following bath A or bath B to form a black film, thereafter chemical treatment as in Example 9 and then coating with the composite resin comprising an organic compound and silica of Example 9 at coverages of 1, 3 and  $5 \text{ g/m}^2$  and then baking treatment to obtain black surface treated steel sheets.

Bath A:  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}/\text{NiSO}_4 \cdot 7\text{H}_2\text{O}/\text{NaNO}_3 = 200/100/5 \text{ g/l}$ ,  $\text{pH} = 1.8$

Bath B: Bath A +  $\text{Na}_5\text{P}_3\text{O}_{10}$   $10 \text{ g/l}$ ,  $\text{pH} = 1.8$

Electrolytic conditions:  $10 \text{ A/dm}^2$ ,  $50 \text{ coulomb/dm}^2$

Chemical treatment: Total deposition amount of chromium  $20 \text{ mg/m}^2$

When bath A was used, the value of L was 19-25 after application of a guard coat and the products were finished in somewhat white color while when bath B was used, the value of L was 12-15 and semigloss appearance was obtained. The coating of the composite resin greatly affected the spot weldability. When it was coated at  $5 \text{ g/m}^2$ , welding was impossible. When it was  $1 \text{ g/m}^2$ , continuous spot welding was possible. When  $3 \text{ g/m}^2$ , failure occurred at the rate of 20%.

Table 6

No.	Materials treated	Aqueous solution (g/l)				pH	Bath temp.	Dk	Q	B-CW
		A	B	C	D					
77	NZ	200	0	10	5	2	40	20	50	2.0
78	"	200	100	5	0	2	"	"	"	2.2
79	"	"	"	2	5	"	"	"	"	1.9
80	"	"	"	"	"	"	"	10	"	1.9
81	"	"	"	3	"	"	"	10	"	1.9
82	"	"	"	4	"	"	"	"	"	2.5
83	"	"	"	"	7	"	"	10	50	1.9
84	"	"	"	"	"	"	"	15	50	1.9
85	"	"	"	"	"	"	"	20	50	2.7
86	"	"	"	5	10	1.9	"	10	50	2.0
87	"	"	"	10	17	1.5	"	10	50	1.9
88	"	"	"	"	"	"	"	20	50	1.9
89	S	"	"	"	"	"	"	10	50	2.6
90	"	"	"	"	"	"	"	"	100	5.5
91	E	"	"	"	"	"	"	"	50	2.2
92	E	"	"	"	"	"	"	"	25	0.9
93	"	"	"	"	"	"	"	"	12	0.3
94	FZ	"	"	"	"	"	"	10	50	2.0

(To be  
cont'd)

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	Guard coat		Value L	Adhesion	Uniformity
	Chemical	Coat			
	Present	Present	25	0	○
	Present	Present	19	30	○
	"	"	19	0	○
	"	"	19	0	○
	"	"	16	0	○
	"	"	17	0	○
	"	"	12	0	○
	"	"	"	0	○
	"	"	"	0	○
	"	"	"	0	○
	"	"	12	0	○
	"	"	"	0	○
	"	"	"	0	○
	"	"	"	0	○
	"	"	13	0	○
	"	"	12	0	○

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A:  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 

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B:  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ C:  $\text{NaNO}_3$ 

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D:  $\text{Na}_5\text{P}_3\text{O}_{10}$ Dk: current density  $\text{A}/\text{dm}^2$ Q: Quantity of current coulomb/ $\text{dm}^2$ 

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B-CW: Deposition amount of black film  $\text{g}/\text{m}^2$ 

Uniformity

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Evaluation of appearance after blackening  
treatment

○ Uniform and beautiful

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Δ Somewhat ununiform

x Ununiform

35

Chemical:  $\text{CrO}_3/\text{SiO}_2$  Total deposition amount  $20 \text{ mg}/\text{m}^2$   
as total chromium

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Coat: Composite film of commercially available  
polyolefin acrylic emulsion and colloidal  
silica ( $1 \text{ g}/\text{m}^2$ )

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Value L: Brightness (JIS Z 8370)  $L \leq 20$  is necessary  
for black

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Adhesion: Erichsen 10 mm drawn and peeling by cellotape.  
Area of peeling is expressed by %.

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Table 7

	Composition of aqueous solution (g/l)									pH	Bath temp.	Dk	Q	B-CW
	A	B	C	D	E	F	G	H	I					
95	200	200	-	-	-	10	-	17	-	2	40	10	50	2.0
96	"	-	200	-	-	"	-	"	-	"	"	"	"	2.1
97	"	200	-	20	-	"	-	"	-	"	"	"	"	1.9
98	"	200	-	-	20	"	-	"	-	"	"	"	"	1.8
99	"	200	-	-	-	10	5	"	-	"	"	"	"	2.0
100	"	"	-	-	-	10	-	-	16	1.8	"	"	"	1.9
101	"	50	50	-	-	5	-	10	-	1.8	"	"	"	1.9
102	"	100	-	-	-	5	-	7	-	3.5	"	"	"	2.5
103	"	"	-	-	-	"	-	"	-	1.8	"	50	"	2.0
104	"	"	-	-	-	"	-	"	-	"	"	70	"	2.5
105	50	100	-	-	-	5	-	10	-	1.8	40	10	50	2.0
106	100	"	-	-	-	5	-	10	-	"	"	"	"	1.9
107	300	"	-	-	-	5	-	10	-	"	"	"	"	2.0

(To be cont'd)

(Cont'd)

	Guard coat		Value L	Adhesion	Uniformity
	Chemical	Coat			
	Present	Present	12	○	○
	"	"	12	○	○
	"	"	13	○	○
	"	"	15	○	○
	"	"	12	○	○
	"	"	13	○	○
	"	"	15	○	○
	"	"	19	Δ ~ ○	Δ
	"	"	12	○	○
	"	"	19	○	Δ ~ ○
	"	"	17	○	Δ ~ ○
	"	"	12	○	○
	"	"	22	○	○

A:  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  B:  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  C:  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  D:  $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ E:  $\text{Cr}_2(\text{SO}_4)_3$  F:  $\text{NaNO}_3$  G:  $\text{KClO}_4$  H: Sodium triphosphosphateI: Sodium hexametaphosphate ( $\text{Na}_8\text{P}_6\text{O}_{19}$ ) ( $\text{Na}_5\text{P}_3\text{O}_{10}$ )

## Example 12

On a 12% Ni-Zn alloy plated steel sheet was formed a black zinc composite plating film by electrolysis in an aqueous sulfate solution of  $\text{Zn}^{2+}/\text{Ni}^{2+}/\text{NaNO}_3 = 45/55/5$  g/l of pH = 2.3 to which was added  $\text{Cr}^{3+}$  in an amount of 0.1 g/l (bath A), 0.5 g/l (bath B) or 1.0 g/l (bath C) at a bath temperature of 40°C, a current density of 30 A/dm<sup>2</sup> and current quantity of 40 coulomb/dm<sup>2</sup> and then a coating type chromate solution composed of silica sol and chromic acid was coated thereon at a total Cr coverage of 30-40 mg/m<sup>2</sup>, followed by drying. Thereafter, thereon was coated a clear resin containing silica by roll coating at a thickness of 1.5 μm and this was baked at 120°C. The value of L was 12 in case of bath A, 13 in case of bath B and 16 in case of bath C. With reference to adhesion, there was recognized no peeling when the samples were subjected to Erichsen test of 10 mm deep drawing. Corrosion resistance according to the salt spray exposure test was 300 hours in case of bath A and 500 hours in case of baths B and C with occurrence of no white rust.

## Example 13

Electrolysis was effected in an aqueous sulfuric acid solution of  $\text{Zn}^{2+}/\text{Ni}^{2+}/\text{NaNO}_3 = 45/55/5$  g/l and pH = 2.3 using a Ni-Zn alloy plated steel sheet as a cathode at a bath temperature of 40°C, a current density of 20 A/dm<sup>2</sup> and a current quantity of 50 coulomb/dm<sup>2</sup>. Then, the sample was dipped in a 1% aqueous condensed phosphoric acid solution for 2 seconds, then washed with water, subjected to a coating type chromate treatment (total Cr coverage 30 mg/m<sup>2</sup>), then coated with a clear resin containing silica at a thickness of 1.5 μm and baked at a sheet temperature of 100°C. The thus obtained colored zinc composite plated steel sheet had black appearance with a value of L = 12, showed no peeling in the Erichsen test of 10 mm drawing, had a corrosion resistance of 300 hours according to the salt spray exposure test and had no white rust.

The color surface treated steel sheet according to this invention is superior in appearance, workability and corrosion resistance and besides has a high resistance to scuffing. This steel sheet can be used in the field of conventional coated steel sheets as a new steel sheet and contributes to production of articles of high quality and low costs.

Further, treating conditions of very wide ranges can be applied and treatment of high speed and short time is possible. Thus, treatment in the conventional electroplating line is possible with low cost.

Especially, this invention has no dependency on the substrate metals for coloration and can easily color the surface through which current is passed. In this respect, this invention is advantageous over the conventional alloy plating method or the method of dissolving an alloy.

## Claims

1. A colored zinc composite-plated steel sheet which comprises a steel sheet or a plated steel sheet, a colored composite-plating film comprising metallic zinc or a zinc alloy and a coloring metal (Me and Zn) oxide or hydrated oxide at a coverage of 0.1-5 g/m<sup>2</sup> provided on said steel sheet and a transparent guard coat having a thickness of 3 μm or less provided on said colored composite-plating film.

2. A colored zinc composite-plated steel sheet according to claim 1 wherein the coloring metal Me is at least one metal selected from the group consisting of Ni, Co, Fe, Cr, Sn and Cu.

3. A colored zinc composite-plated steel sheet according to claim 1 wherein the guard coat comprises a chemical treatment film, resin film, inorganic polymer film, composite film of an inorganic polymer and a resin, oil, fat, wax or combination thereof.

4. A colored zinc composite-plated steel sheet according to claim 3 wherein the chemical treatment film is a chromate film, a phosphate film or a chelate film.

5. A colored zinc composite-plated steel sheet according to claim 3 wherein the chemical treatment film is a chromate film containing phosphoric acid.

6. A colored zinc composite-plated steel sheet according to claim 3 wherein the resin film contains a chromium compound, an oxide selected from silica, titania, alumina and zirconia, a silicate mineral selected from mica and talc, an inorganic compound selected from a phosphate and a borate, a fatty acid soap, carbon, a fatty acid ester, plastic particles, a silane coupling agent and/or a titanium coupling agent.

7. A colored zinc composite-plated steel sheet according to claim 1 wherein the steel sheet or the plated steel sheet is gloss finished with an average surface roughness of 1.0 μm or less.

8. A colored zinc composite-plated steel sheet according to claim 1 wherein the steel sheet or the plated steel sheet is semigloss finished with an average surface roughness of  $1.5\text{ }\mu\text{m}$  or more.

9. A colored zinc composite-plated steel sheet according to claim 1 which comprises the colored composite-plating film mainly composed of zinc and a coloring metal oxide provided on said steel sheet or plated steel sheet at a coverage of  $0.5\text{--}2.0\text{ g/m}^2$ , a chromate film provided on said film and a composite film comprising silica and an organic resin having a thickness of  $0.5\text{--}2\text{ }\mu\text{m}$  provided on said chromate film.

10. A colored zinc composite-plated steel sheet according to claim 1 wherein the colored composite-plating film contains a condensed phosphate.

11. A method for making a colored zinc composite-plated steel sheet which comprises effecting electrolysis in an acidic aqueous solution mainly composed of  $\text{Zn}^{2+}$  ions, coloring metal ions  $\text{Me}^{n+}$  and strongly oxidizing ions  $\text{OX}^-$  using a steel sheet or a plated steel sheet as a cathode to form a colored composite-plating film mainly composed of zinc and a coloring metal oxide or hydrated oxide at a coverage of  $0.1\text{--}5\text{ g/m}^2$  on said steel sheet or plated steel sheet and then applying a transparent guard coat having a thickness of  $3\text{ }\mu\text{m}$  or less onto said film.

12. A method according to claim 11 wherein the colored composite-plating film formed is subjected to chemical treatment and then provided with the guard coat.

13. A method according to claim 11 wherein the coloring metal ion  $\text{Me}^{n+}$  is at least one ion selected from the group consisting of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Sn}^{2+}$ , and  $\text{Cu}^{2+}$ .

14. A method according to claim 11 wherein the strongly oxidizing ion  $\text{OX}^-$  is at least one ion selected from the group consisting of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{ClO}_4^-$  and  $\text{ClO}_3^-$ .

15. A method according to claim 11 wherein a solution containing at least one ion selected from the group consisting of  $\text{P}_2\text{O}_4^{4-}$ ,  $\text{P}_3\text{O}_{10}^{5-}$ ,  $\text{P}_4\text{O}_{13}^{6-}$  and  $\text{P}_6\text{O}_{19}^{8-}$  is used.

16. A method according to claim 11 wherein the acidic aqueous solution has a pH of 1-4.

17. A method according to claim 10 wherein the concentration of  $\text{Zn}^{2+}$  is  $10\text{--}100\text{ g/l}$ , that of the coloring metal ion is  $10\text{--}100\text{ g/l}$  and that of the strongly oxidizing ion is  $1\text{--}50\text{ g/l}$ .

18. A method according to claim 11 wherein the concentration of  $\text{Zn}^{2+}$  is  $20\text{--}50\text{ g/l}$ , that of the coloring metal ion is  $20\text{--}70\text{ g/l}$  and that of the strongly oxidizing ion is  $1\text{--}20\text{ g/l}$ .

19. A method according to claim 11 wherein concentration of  $\text{Zn}^{2+}$  is  $10\text{--}100\text{ g/l}$ , that of the coloring metal ion is  $10\text{--}100\text{ g/l}$  and that of the strongly oxidizing ion is  $1\text{--}50\text{ g/l}$  and that of  $\text{Cr}^{3+}$  is  $0.1\text{--}10\text{ g/l}$ .

20. A method according to claim 11 wherein the acidic aqueous solution has a ratio  $\text{Me}^{n+}/\text{Zn}^{2+}$  of  $0.1\text{--}1.0$ .

21. A method according to claim 11 wherein the acidic aqueous solution has a ratio  $\text{Me}^{n+}/\text{Zn}^{2+}$  of 1 or more.

22. A method according to claim 11 wherein the acidic aqueous solution has a ratio  $\text{Me}^{n+}/\text{Zn}^{2+}$  of  $1.5\text{--}3.0$ .

23. A method according to claim 11 wherein the electrolysis is effected at a current density of  $10\text{--}100\text{ A/dm}^2$  and a current quantity of  $20\text{--}200\text{ coulomb/dm}^2$ .

24. A method according to claim 11 wherein the electrolysis is effected at a current density of  $5\text{--}50\text{ A/dm}^2$  and a current quantity of  $5\text{--}100\text{ coulomb/dm}^2$ .

25. A method according to claim 11 wherein the electrolysis is effected at a current density of  $5\text{--}100\text{ A/dm}^2$  and a current quantity of  $20\text{--}200\text{ coulomb/dm}^2$ .

26. A method according to claim 11 wherein temperature of the acidic aqueous solution is  $20\text{--}60^\circ\text{C}$ .

27. A method according to claim 11 wherein the colored zinc composite-plating film is formed at  $0.1\text{--}5\text{ g/m}^2$ , then treated with an aqueous solution of a phosphoric acid compound and then subjected to a chromate treatment and guard coating in a thickness of  $3\text{ }\mu\text{m}$  or less.

FIG. 1

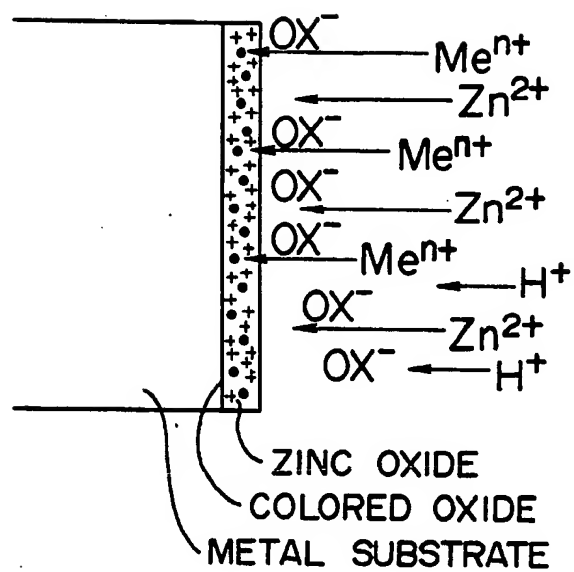


FIG. 2(a)

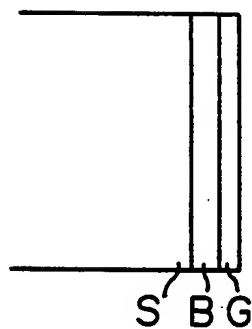


FIG. 2(b)

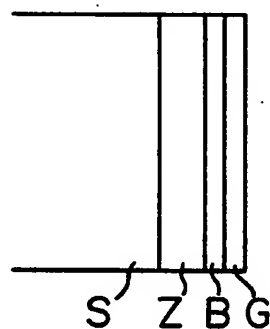


FIG. 2(c)

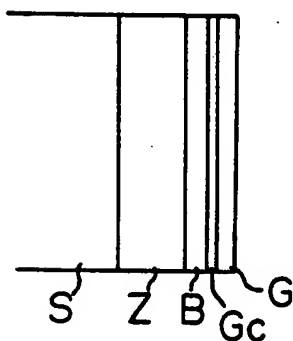


FIG. 2(d)

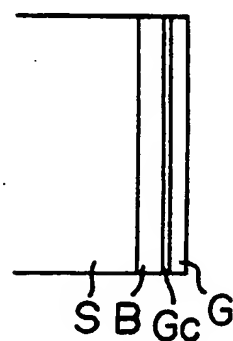
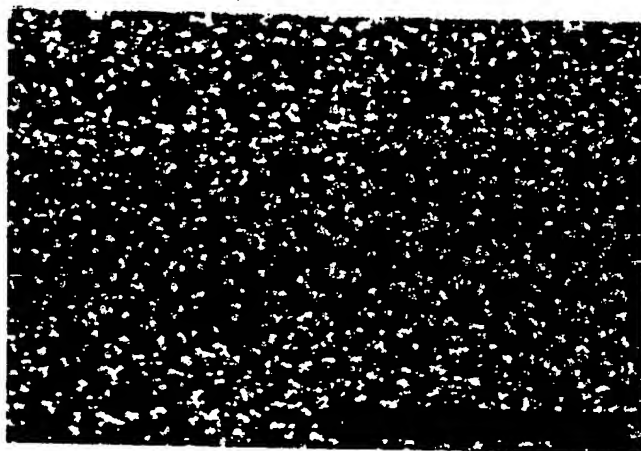


FIG. 3



x 3500

FIG. 4



x 3500



European Patent  
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## EUROPEAN SEARCH REPORT

Application number

EP 87111905.3

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 9, no. 271, October 29, 1985  THE PATENT OFFICE JAPANESE GOVERNMENT page 135 C 311  * Kokai-no. 60-121 275 (SUMITOMO) *  --	1,3,4, 11,14	B 32 B 15/18 C 25 D 9/08 C 25 D 9/10 C 23 C 28/00 C 25 D 11/26
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P,A	AT - B - 381 278 (ZINCROKSID)  * Abstract *  --	1,2,11 13	TECHNICAL FIELDS SEARCHED (Int. Cl.4) B 32 B 15/00 C 25 D C 23 C
A	DE - A1 - 3 028 587 (TEKSID)  * Claims *  --	1,2,11 13	
A	DE - A1 - 3 329 745 (ZINCROKSID)  * Abstract *  ----	1,2,11 13	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 18-12-1987	Examiner ONDER
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  & : member of the same patent family, corresponding document	